A COMBINED LASER ABLATION - RESONANCE IONIZATION MASS SPECTROMETER FOR PLANETARY SURFACE GEOCHRONOLOGY

G. Cardell[1], M. E. Taylor[1], B. W. Stewart[2], R. C. Capo[2], and D. A. Crown[2,3]
[1]In Situ Technology & Experiments Systems Section, MS 302-231, Jet Propulsion Laboratory, Pasadena CA 91109
[2]Department of Geology & Planetary Science, University of Pittsburgh, Pittsburgh PA 15260
[3]Planetary Science Institute, 620 N. 6th Ave., Tucson, AZ 85705

Introduction

A primary objective in studies of solar system evolution is to delineate the timing of geologic processes that shape the surfaces of planetary bodies [1]. Absolute dating of rocks exposed on or near the surface of other planets is currently accomplished only through analysis of returned samples or meteorites in terrestrial geochemistry laboratories. An in situ geochemistry instrument capable of determining the ages of rocks on planetary surfaces is a leading technology for solar system science. Recent technological advances indicate that such an instrument is feasible. We have formed an interdisciplinary team with expertise in the areas of planetary science, Mars surface geology, radiogenic isotope geochemistry, and advanced instrument engineering. Our approach is to integrate currently available instrumentation, existing laboratory techniques, and recent developments in photonics to construct a laboratory breadboard instrument capable of directly determining the crystallization age of a rock using the rubidium-strontium isotope decay system. This breadboard instrument will form the basis for a miniature in situ geochronology instrument for planetary surface deployment.

Martian Chronology

Remote sensing of planets such as Mars can provide an important relative chronology of major events, but absolute time scales are currently established only by indirect methods such as impact crater densities, and epoch boundary age uncertainties are as high as 2 Ga in some cases. Meteorites thought to be of Martian origin indicate an extended geologic history for the planet, with ages ranging from ~4.5 Ga to ~0.16 Ga, and the recent suggestion that the oldest of the Martian meteorites contains fossil evidence of life has spurred a renewed interest in the evolution of Mars [2]. An approach that combines Rover-based in situ surface sensors with sample return has the potential to greatly enhance our understanding of Mars.

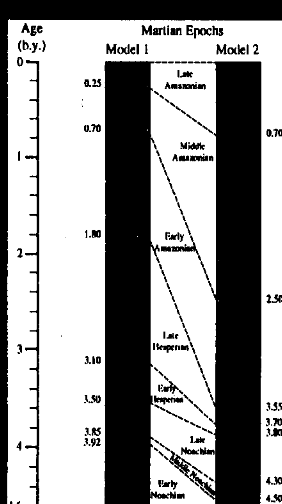
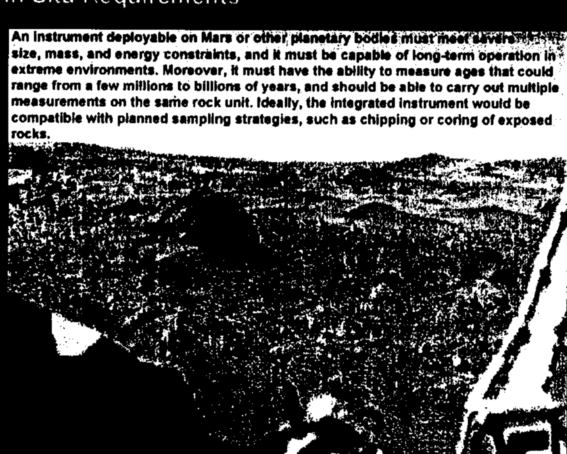


FIG 1. Two models for Martian epoch boundaries, modified from Tanaka et al. [3]

In Situ Requirements

An instrument deployable on Mars or other planetary bodies must meet severe size, mass, and energy constraints, and it must be capable of long-term operation in extreme environments. Moreover, it must have the ability to measure ages that could range from a few millions to billions of years, and should be able to carry out multiple measurements on the same rock unit. Ideally, the integrated instrument would be compatible with planned sampling strategies, such as chipping or coring of exposed rocks.



Rubidium-Strontium System

The basis of the Rb-Sr system is the decay of ^{87}Rb to ^{87}Sr by β – emission with a half-life of 48.8 Ga. An age is obtained by measuring the $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios of two or more rocks or minerals, generally igneous, thought to be thermally and isotopically equilibrated at time zero, i.e. during crystallization.

A number of other isotope systems have appropriate half lives and partitioning behavior for Martian geochronology, including the K-Ar, Sm-Nd, and U-Th-Pb systems. We are currently focusing on the Rb-Sr system for in situ geochronology on the surface of Mars and other rocky planetary bodies for the following reasons. However, the instrument design concept could be adapted to other isotope systems as well.

- The Rb-Sr decay constant is ideal for the age range measured for SNC meteorites and has been used successfully on a wide range of extraterrestrial materials.
- Rb and Sr are typically present in rock-forming minerals in concentrations greater or equal to the concentrations of members of other systems.
- Rb and Sr are not readily mobilized after incorporation into rock-forming minerals.
- There are few isobaric interferences in the Rb-Sr mass range.
- Necessary measurements can be made simultaneously using a multichannel detector.
- Rb and Sr have relatively low ionization energies.

Measurement Precision

The primary challenge is to achieve the required accuracy and precision in measuring $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios. Figure 2 shows a two-point isochron for minerals that are likely to be found on the surface of Mars. The age is calculated from the slope of the correlation, so the uncertainty in the age is related to the uncertainty in the slope. Figure 3 shows the measurement uncertainty required for age uncertainties of 0.5 Ga or less. The calculations are for a two-point isochron; additional points could reduce the calculated age uncertainty. As indicated, ages good to ±0.5 Ga or better could be obtained with ratio measurements far less precise than those achievable by terrestrial instruments.

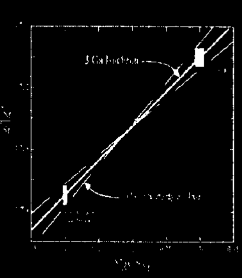


FIG 2. Theoretical two-point isochron for plagioclase feldspar and clinopyroxene, two minerals likely to be found in Martian igneous rocks.

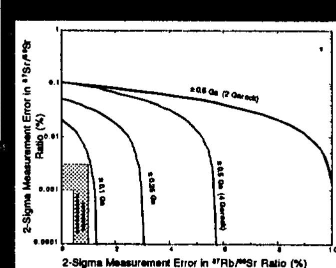
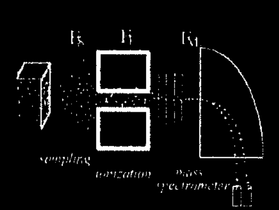


FIG 3. Calculated uncertainties in measured isotope ratios necessary to achieve indicated uncertainties in ages for two-point isochrons.

Measurement precision is a function of the number of ions that are measured, which in turn, is a function of the sampling, ionization, and mass spectrometer efficiencies, as shown in Figure 4. For reference, Figure 5 shows the relationship between the number of Sr ions measured and the uncertainty in the measured $^{87}Sr/^{86}Sr$ ratio for a thermal ionization mass spectrometer system.



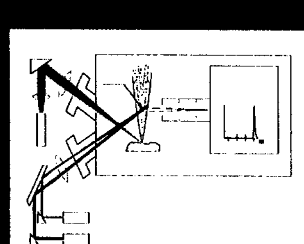
$$E_T = E_S \cdot E_I \cdot E_M$$

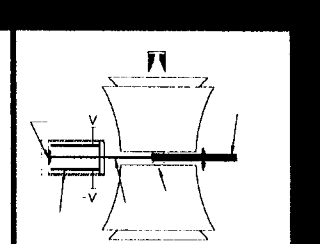
FIG 4. Total efficiency is the product of the sampling, ionization, and mass spectrometer efficiencies.

FIG 5. Relationship between number of ions and measurement uncertainty for a thermal ionization mass spectrometer system.

Instrument Concept

In order to obtain an age using the parent-daughter systems described above, an in situ geochronology instrument must be capable of measuring isotope concentrations in multiple mineral crystals from a single rock. The instrument we are developing will use advanced laser and miniature mass analysis technology to implement the sample preparation, ionization, and mass analysis in three closely integrated steps using laser ablation sampling, resonance ionization, and ion trap mass spectrometry. These stages currently exist or are under development at the Jet Propulsion Laboratory.





FIGS 6&7. Schematics showing instrument concept and possible instrument geometries.

References

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Progress

I. Laser Ablation Sampling

Minerals (targets) were ablated in vacuum at 266 nm and 355 nm, and ablation products (films) were collected on carbon, teflon, and silicon substrates. The compositions of the targets and films were then compared to quantify fractionation. Chemical fractionation of major elements, analyzed using Rutherford backscattering spectrometry and x-ray photoelectron spectroscopy, was found to occur in predictable and reproducible ways [4]. A study of chemical and isotopic fractionation of Rb and Sr is now underway using conventional thermal ionization mass spectrometry.

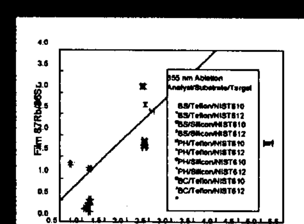

FIG 8. Film $^{87}Rb/^{86}Sr$ ratios versus target $^{87}Rb/^{86}Sr$ ratios for 355 nm ablation.

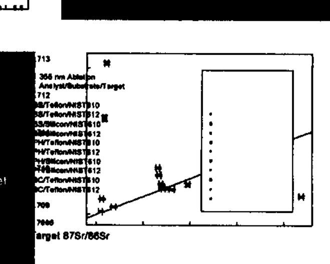

FIG 9. Film $^{87}Sr/^{86}Sr$ ratios versus target $^{87}Sr/^{86}Sr$ ratios for 355 nm ablation.

II. Resonance Ionization

A low-power diode-laser compatible resonance ionization scheme for Sr has been demonstrated on thermally evaporated Sr atoms. A similar scheme for Rb is under development.

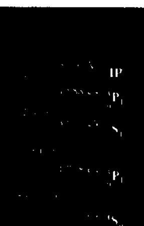

FIG 10. Sr resonance ionization scheme.

III. Ion Trap Mass Spectrometry

A miniature ion trap mass spectrometer optimized for combined laser ablation sampling and resonance ionization was designed and constructed. The split ring electrode provides near 360° access for the ablation laser and the resonance ionization lasers and permits direct capture of ablation plumes. The ion storage feature allows averaging of of multiple sampling events, compensating for laser and sample variations. Experiments will be performed at a variety of pressures and background gases to determine the optimal working conditions.

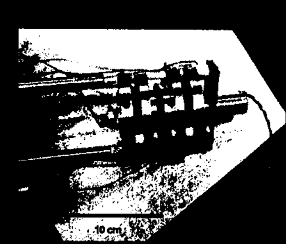

FIG 11. Ion trap mass spectrometer.

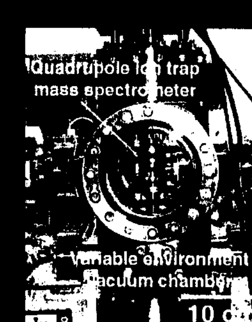

FIG 12. Ion trap mass spectrometer in variable environment vacuum chamber.

V. Integration

A breadboard instrument which integrates laser ablation sampling, resonance ionization, and ion trap mass spectrometry is now under development.

Summary

Results to date indicate that an in situ geochronology instrument based on theRb-Sr system is a viable concept. Work in progress includes laser ablation sampling of natural minerals, removal of natural ions by electrostatic deflection, resonance ionization ofRb and Sr atoms, and mass detection ofRb and Sr ions.